

Ether Alcohol Sulfates from Oleyl Alcohol¹

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Abstract

Oleyl alcohol was caused to react with ethylene oxide, propylene oxide, and 1,2-butylene oxide in the presence of an alkaline catalyst. The first and second derivatives from each reaction were isolated by fractional distillation. Sulfation with dioxane-SO₃ gave high-purity oleyl ether sulfates, easily soluble, with good detergent and lime soap-dispersing properties.

The use of chlorosulfonic acid or sulfuric acid as the sulfating agent for oleyl ether alcohols resulted in about 60% retention of the double bond, compared with oleyl alcohol, which under the same conditions retained only about 25% unsaturation. Oleyl ether alcohols sulfated with chlorosulfuric acid or sulfuric acid are easily soluble and have good lime soap-dispersing properties. They are able to solubilize less soluble soaps and saturated ether alcohol sulfates.

Introduction

PREVIOUS STUDY of the oxyalkylation and sulfation of saturated tallow alcohols (6) has shown that higher yields of mono-oxyalkylated product are obtained with propylene oxide and butylene oxide than with ethylene oxide. Also the sulfation products are more soluble than those from ethylene oxide, which in turn are more soluble than the parent sodium alkyl sulfates.

Under some conditions it may be more desirable to oxyalkylate tallow alcohol in which unsaturation is present. Investigation has now been extended to the oxyalkylation and sulfation of oleyl alcohol, comparing the effect of oxyalkyl groups on the sulfation process and measuring the surface-active properties of the unsaturated tallow ether alcohol sulfates.

Experimental Section

Materials

A commercial oleyl alcohol was distilled, and the major fraction was dissolved in acetone (4 cc/g) and crystallized at -10°C. The solid saturates were discarded, the filtrate was diluted (8 cc/g), twice crystallized at -45°C, and distilled again through a 2-ft column which was packed with 0.16 in. stainless steel protruded packing. The major fraction b_{0.07} 124-126°C, was found to be 99% pure by GLC: IV 94.2 (theory 94.5); % OH 6.42 (theory 6.34).

Elaidyl alcohol was prepared by elaidinization of oleyl alcohol with Se and purified by crystallization and distillation (5): found, IV 92.2; mp 35°C.

Epoxides were high-purity samples described in a previous publication (6).

Oxyalkylation

Reaction with propylene oxide and butylene oxide was carried out at 160°C in the presence of 0.5% KOH catalyst as described previously (6). Reaction with ethylene oxide was similar except that the epoxide was not returned to the reaction by reflux. A

gaseous stream of ethylene oxide was led into the unsaturated alcohol, and the extent of reaction was determined by weight increase.

Distillation

Reaction products were separated by distillation at 0.3 mm pressure through a 1-ft column filled with 0.24 in. stainless steel protruded packing. A capillary N₂ bleed was used.

Gas-Liquid Chromatography

Vapor-phase chromatographic analysis was carried out on an F & M 810 dual column chromatograph, fitted with 8-ft 20% SE 30 silicone gum rubber columns, operating isothermally at 280°C. The thermal conductivity detection system was used. Mixtures of ether alcohols were analyzed after conversion to the acetates.

Sulfation

Three different sulfation procedures were used and compared.

Method I was used to prepare pure ether alcohol sulfates with a minimum of reaction at the double bond. Dioxane-SO₃, used in slight excess, was prepared by adding liquid SO₃ to a cold, stirred solution of purified dioxane in CCl₄. The ether alcohol was then added to the cold slurry of the sulfating complex, and the reactants were warmed to 45°C. The mixture was cooled again, diluted with cold ethanol, neutralized with 18 N NaOH, and twice crystallized from ethanol at -25°C to give a product the purity of which was confirmed by iodine number and analysis for sodium. Yields of purified products were 40-70% with 95-98% double bond retention.

Method II was the same as that used for the sulfation of saturated ether alcohols (6). A 10% molar excess of ClSO₃H was added dropwise to a stirred solution of ether alcohol in cold CCl₄. The reaction was warmed to room temperature, cooled again, diluted with cold ethanol, and neutralized with 18 N NaOH. Most of the CCl₄ was boiled off, the residue was taken up in 95% ethanol and crystallized. Yields

TABLE I
Oleyl^a and Elaidyl^b Ether Alcohols

	i	Purity by GLC %	Freezing point °C	²⁰ n _D
R(OCH ₂ H ₄) ₁ OH	1	99.8	-1	1.4608
from ethylene oxide	2	97.7	+5.5	1.4614
R(OCH ₂ CH) ₁ OH	1	99.3	-16	1.4580
from propylene oxide	2	96.7	-30	1.4563
R(OCH ₂ CH) ₁ OH	1	99.9	-9	1.4580
from butylene oxide	2	99.9	-32	1.4572
R'(OCH ₂ CH) ₁ OH	1	99.9	+24	1.4580 ^c

^a R.

^b R'.

^c Supercooled.

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and double bond retention are compared in Table III. Unsaturation was determined, before and after crystallization by the Wijs method, with acetic acid as the only solvent.

Method III was the use of 100% H_2SO_4 for the sulfation of oleyl alcohol and monoöxypropylated oleyl alcohol. Sulfuric acid, 0.09 moles, brought to 100% by adding liquid SO_3 to concentrated H_2SO_4 , was added dropwise to a stirred mixture of 0.06 moles of the alcohol in an equal volume of CCl_4 . The temperature was slowly raised to 50C. After cooling again to 0C and dilution with ethanol the product was neutralized with 18 N NaOH and crystallized in the same manner as the ClSO_3H product. Yields of crystallized product from H_2SO_4 sulfation were 35-45%.

Synthetic Tallow Mixtures

Banks and Hilditch (1) found a North American beef tallow to have the fatty acid composition of 6.3% myristic acid, 27.4% palmitic acid, 14.1% stearic acid, 49.5% oleic acid, and 2.4% linoleic acid. Oxypropylated or oxybutylated alcohol sulfates from tallow should therefore contain 6.8% tetradecyl, 28.1% hexadecyl, and 13.9% octadecyl derivatives, as well as 51.2% unsaturated 18 carbon derivatives, which will be considered as the oleyl derivative. Monoöxypropylated and monoöxybutylated tallow alcohol sulfates were prepared by mixing chlorosulfonic acid sulfation products in the above proportions. A synthetic monoöxybutylated hydrogenated tallow alcohol sulfate was made in the same way from 6.8% $\text{C}_{14}\text{H}_{29}\text{OC}_4\text{H}_8\text{OSO}_3\text{Na}$, 28.1% $\text{C}_{16}\text{H}_{33}\text{OC}_4\text{H}_8\text{OSO}_3\text{Na}$, and 65.1% $\text{C}_{18}\text{H}_{37}\text{OC}_4\text{H}_8\text{OSO}_3\text{Na}$. Data on these mixtures are given in Table IV.

Measurement of Surface-Active Properties

Detergency and other surface-active properties were

TABLE II
Surface-Active Properties of Pure Ether Alcohol Sulfates^a

Sulfate	Solubility ^b	cmc ^c milli- moles per liter	Lime soap- dis- persing power (2) %	Foam height (4), 0.25% built solu- tion ^d 60C, 300 mm. ppm	Detergency, ΔR^e , 60C 0.1% un- built 100 ppm
Sodium 2-oleloxyethyl sulfate	5	0.15	8	180	28
Sodium 2-oleloxy-1-methylethyl sulfate	2	0.12	9	170	28
Sodium 2-oleloxy-1-ethylethyl sulfate	5	0.11	12	130	27
Sodium oleyl sulfate	10	0.29	10	195	27
Sodium 2-octaacyloxyethyl sulfate	(Krafft point 46°)	0.11	9	100	29
Sodium octadecyl sulfate	(Krafft point 56°)	0.11 ^f	(see g)	190	28
Sodium dodecyl sulfate	40 (Krafft point 16°)	6.8	30	185	18

^a Sulfation with dioxane— SO_3 .

^b Concentration, %, at which the solution becomes noticeably viscous.

^c Critical micelle concentration, Pinacynole Chloride titration.

^d Built solutions are 0.05% with respect to active ingredient, 0.2% with respect to builder of the following composition: 55% $\text{Na}_2\text{P}_2\text{O}_7$, 24% Na_2SO_4 , 10% $\text{Na}_4\text{P}_2\text{O}_7$, 10% Na metasilicate, 1% CMC.

^e ΔR = increase in reflectance after washing standard soiled cotton (3) in the Terg-O-Tometer for 20 min, 110 cpm.

^f Measured at 60C.

^g Not soluble enough for the test conditions.

TABLE III
Sulfation of Oleyl and Elaidyl Ether Alcohols^a with Chlorosulfonic Acid

	Mole ratio $\text{ClSO}_3\text{H}/\text{Alcohol}$	Total double bond retention %	Crystallized product	
			Yield %	Double bond retention %
$\text{ROC}_2\text{H}_4\text{OH}$	1.16	61	78	71
$\text{ROC}_3\text{H}_5\text{OH}$	1.18	(see ^b)	71	73
$\text{R}(\text{OC}_3\text{H}_5)_2\text{OH}$	1.32	60	(see ^c)	(see ^c)
$\text{ROC}_4\text{H}_7\text{OH}$	1.12	68	54	80
$\text{R}'\text{OC}_3\text{H}_5\text{OH}$	1.21	51	64	69
ROH	1.01	27	71	27
ROH	2.03	(see ^b)	82	4

^a R = oleyl, R' = elaidyl.

^b Data not available.

^c Product could not be crystallized.

measured as in the previous publication (6). Lime soap-dispersing power was measured by the method of Borghetty and Bergman (2) and foam height by the Ross-Miles test (4). Critical micelle concentration was measured by the Pinacynole Chloride dye titration method, and Krafft point as the temperature at which a 1% dispersion became clear on gradual heating. Detergency was measured as the increase in reflectance after washing 10 swatches of standard soiled cotton in one liter of detergent solution in the Terg-O-Tometer for 20 min at 60C and 100 cpm. The results are recorded in Tables II and IV.

Results and Discussion

Oleyl alcohol reacts with ethylene, propylene, and butylene oxides in the same manner as the saturated alcohols. Figure 1 compares the disappearance of the parent alcohol, and Figure 2 compares the yield of first derivative with increasing additions of ethylene oxide and butylene oxide. Analyses were by GLC of the acetates, confirmed in several cases by fractional distillation and separation of the parent alcohol and the first and succeeding derivatives. It can be seen that butylene oxide consumes oleyl alcohol much more rapidly, and higher yields of the first derivative result. The distribution constant, or ratio of ether alcohol reactivity to parent alcohol reactivity, is about 2 for the ethylene oxide reaction, 0.5 for the propylene oxide, and 0.3 for butylene oxide. The "constant" changes at low additions of eth-

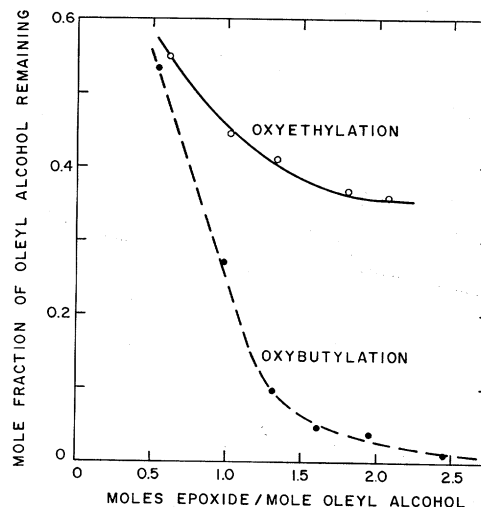


Fig. 1. Disappearance of oleyl alcohol with increasing additions of epoxide:

—○— for the ethylene oxide reaction
--○-- for the butylene oxide reaction.

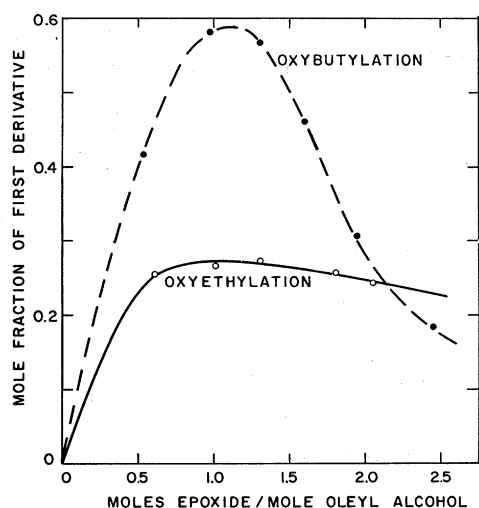


FIG. 2. Yield of first derivative with increasing additions of epoxide:

—○— mole fraction of $C_{18}H_{35}OCH_2CH_2OH$
 --●-- mole fraction of $C_{18}H_{35}OCH_2CH(C_2H_5)OH$.

ylene oxide, as has been reported by Weimer and Cooper (7), but it is truly constant for propylene oxide and butylene oxide reactions. For ethylene oxide the high value of the reactivity ratio and its

TABLE IV
Detergent Properties of Unsaturated Ether Alcohols Sulfated with Chlorosulfonic Acid

	Krafft ^a point 1% °C	Lime soap- dis- persing power (2) %	Foam height (4) 0.25% built ^b 60C, mm	Detergency, ΔR°, 60C	
				0.25% built ^d 300 ppm	0.1% unbuilt, 100 ppm
Monoöxyethylated oleyl alcohol	Clear at zero	7	170	28	25
Monoöxypropylated elaidyl alcohol	Clear at zero	8	160	28	24
Monoöxypropylated oleyl alcohol	Clear at zero	10	155	27	17
Dioxypropylated oleyl alcohol	Clear at zero	7	150	26	18
Monoöxybutylated oleyl alcohol	Clear at zero	10	150	27	21
Oleyl alcohol	Clear at zero	18	175	27	23
Monoöxypropylated tallow alcohol	27	9	150	27	26
Monoöxybutylated tallow alcohol	24 ^d	10	150	26	20

^a Temperature at which a 1% dispersion becomes clear on gradual heating.

^b Built solution 0.05% active ingredient + 0.20% builder of the following composition: 55% $Na_4P_2O_{10}$, 24% Na_2SO_4 , 10% $Na_4P_2O_7$, 10% Na metasilicate, 1% CMC.

^c ΔR = increase in reflectance after washing standard soiled cotton (3) in a Terg-O-Tometer, 20 min, 110 cpm.

^d Krafft point of sulfated monoöxybutylated hydrogenated tallow alcohol = 36°.

increase with the increase in the mole ratio of ethylene oxide combines to give the nearly constant analysis for monoöxyethylated product shown in Figure 2.

Properties of the individual ether alcohols separated from reaction mixtures by fractional distillation are shown in Table I. Purity was confirmed by GLC, iodine value, and % hydroxyl. Lack of a sharp absorption peak in the 960 cm^{-1} region indicates the absence of *trans* isomers.

The solubility and surface properties of pure unsaturated ether alcohol sulfates made from the ether alcohols of Table I by sulfation with dioxane- SO_3 are shown in Table II. The ether alcohol sulfates from oleyl alcohol, like those from octadecanol, are good detergents and lime soap-dispersing agents. They have somewhat better foaming properties and are more soluble in water and organic solvents. Sodium 2-olexyloxy-1-ethylethyl sulfate, $C_{18}H_{33}OCH_2CH(C_2H_5)OSO_3Na$, in particular, readily forms clear 2% solutions in CCl_4 , $(C_2H_5)_2O$, petroleum ether, petrolatum and $C_6H_5CH_3$.

Table III shows that sulfation with $ClSO_3H$ (Method II) is best accomplished with about a one molar ratio. Ether alcohols are sulfated with greater retention of the double bond (70–80%) than in the case of oleyl alcohol (27%), presumably because the ether alcohol tends to form a complex with $ClSO_3H$ and so moderates its activity and directs the reaction primarily to the hydroxyl group. Analysis of the crystallized reaction product, for % Na and I.V., shows that disulfation does not occur. Double bond retention is about the same for *cis* or *trans* isomers, or mono- or dioxyalkylation.

With 100% H_2SO_4 as the sulfating agent (Method III), monoöxypropylated oleyl alcohol was sulfated with a 40% yield of crystallized product and 70% double bond retention. Apparently H_2SO_4 also tends to form a complex with the ether alcohol.

The chlorosulfonic acid reaction products of Table IV have properties like the pure ether alcohol sulfates of Table II. All are good lime soap-dispersing agents and good detergents in built systems. The detergency data at 0.1% concentration, unbuilt, in water of 100 ppm shows differences between the individual detergents.

The monoöxypropylated and oxybutylated tallow alcohol sulfates have good properties and are easily soluble because the more soluble components solubilize the less readily soluble. For example, monoöxybutylated tallow alcohol sulfate has a Krafft point of 24C compared with 36C for a similar product from hydrogenated tallow alcohol.

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